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(54) A Multi-layer System for Heat Protective Applications

(57) A multi-layer heat protective structure exhibiting improved corrosion resistance e.g. for use in windows comprises a carrier 21 e.g. of polyester foil overlaid by a metal layer 25 which may be sprayed silver, and further including one or more dielectric layers such as TiO_2 layers 22, 24, 26, 28 and pure TiN or TiO_2/TiN mixture layers 23, 27, at least one of the dielectric layers necessarily including a metal nitrogen compound. The dielectric layers may be applied by reactive magnetron atomization in an atmosphere including Ar, O_2, N_2. A de-mirroring layer 32 (Figure 3) of magnesium fluoride may be applied to the back of the foil 31 whereby transmission factors of 88% are achieved in the visible and near i.r. range compared to a reflective capacity of about 95% in the far i.r.

FIG.2

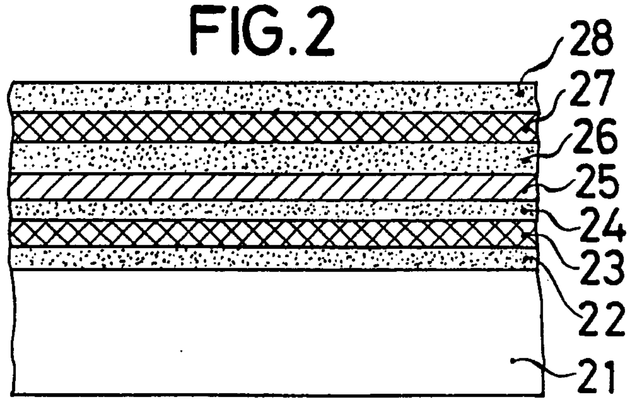

FIG.3

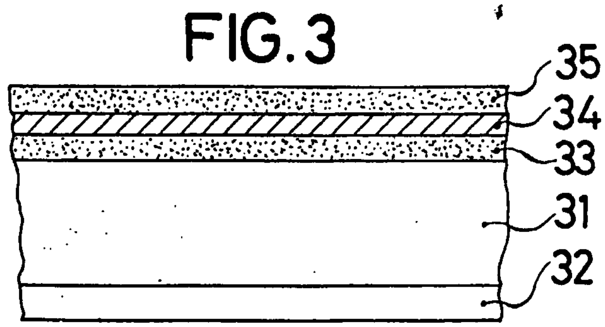

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FIG.1

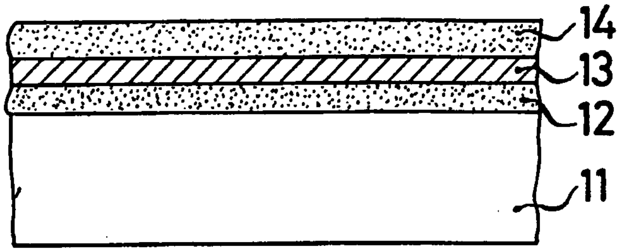


FIG.2

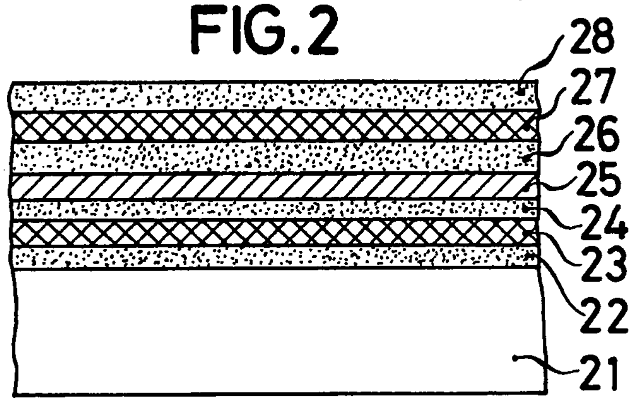
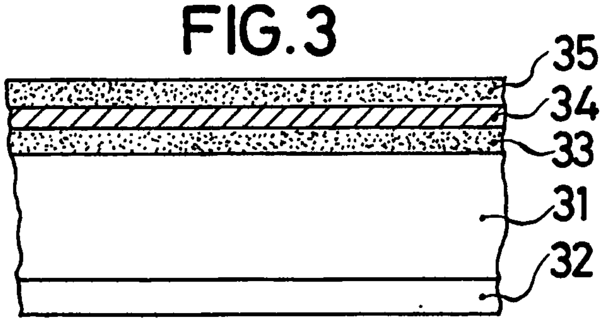


FIG.3



SPECIFICATION

A Multi-layer System f r Heat Protecti n Applications and a Method for Its Producti n

State of the Art

The invention originates from a multi-layer system according to the preamble to the main claim. Solar protective foils are known which are fitted in summer as solar protection in the region of the window and prevent excessive heating of the interior of the room by reflection of the solar radiation.

Heat protective devices are also known which offer a protection in winter against heat radiation from the interior of the room to the outside (German OS 27 03 688) and thus lead to a reduction in the coefficient of heat transmission and the heat losses from the interior of the room to the outside.

Both the solar protection device and the heat protection device are based on the principle of the reflection of radiation at a metal film, for example vapour deposited on a backing foil. Moreover, the transmission factor of a thin metal layer can be increased in the visible spectral range by a demirroring layer. Thus, multiple layer systems consisting of metallic and dielectric layers are known. Moreover, silver, gold, aluminium and copper are used predominantly as metals. The dielectric, that is to say non-conducting layers, are highly refractive metal oxides, such as for example TiO_2, SiO_2, Ti_2O_3, Ta_2O_5, ZrO_2 or metal sulphides such as for example ZnS. These multi-layer systems are applied to plastics foils or glass backings and are used for the purpose of heat protection or area heating. Heat protective devices need a high transmission factor in the visible spectral range and a high reflective capacity for infrared radiation (far infrared, $\lambda \approx 10$ microns), that is to say for heat radiation from the interior of the room.

Advantages of the Invention

The application of multi-layer systems in accordance with the invention results from the following reasons:

First of all, the electrically conducting metal layer producing the infrared reflection must have better properties of adhesion to the substrate. Furthermore, the dielectric layers provide good protection against corrosion by covering the metal layer on both sides. However, the metal layer can also be applied directly to the carrier foil or to glass, possibly with pre-glueing, and be provided with a cover layer on only one side.

The transparency of the metal layer depends on the reflective capacity in the visible spectral range. The reflection capacity is a function f the coefficient of refraction of the material. The applied m tal layer has a relatively high reflectiv capacity (high refractive ind x) in the visible spectral range. Thus, its transmissi n factor is n t first of all satisfactory for the desired applicati n.

By adaptation of the dielectric c ver layer with respect to its refractive ind x (in the ideal case $n_{air}:n_{cover\ layer}=n_{cover\ layer}:n_{metal}$) and with it the intensity of the reflection and after adaptation of its layer thickness ($2\Delta=\lambda/2$; 2Δ=path length of the reflected radiation in the cover layer) interference phenomena occur in the visible spectral range, that is to say the reflection at the metal layer and at the dielectric layer compensate mutually in the ideal case. The transmission factor in the visible spectral range of the multi-layer system is increased thereby. Nevertheless, the dielectric cover layer is of advantage for increasing the transmission factor. With known cover layers, metal nitrides are not used in the field of optical application since, in a pure form, these have an insufficient transmission factor in the visible range.

As opposed to the known systems, the arrangement in accordance with the invention comprising the characterising features of the main claim has the advantage that a distinct improvement in known multi-layer systems is provided as regards the resistance of the entire layer system to external influences, especially mechanical, chemical and electro-chemical influences, without the transmission capacity in the visible spectral range being impaired. Thus, with the multi-layer system in accordance with the invention, an improvement in the properties is achieved against corrosion phenomena. In particular, a better resistance to the action of gaseous and liquid media is also achieved by the multi-layer system in accordance with the invention. This improvement is achieved *inter alia* by the incorporation of metal nitrides in the cover layer without the transparency being markedly impaired thereby.

The heat protective system in accordance with the invention has a high transmission capacity (D>80%) in the visible and near infrared spectral range (λ=0.4 to 1.4 um), whilst in this range of wavelengths the reflective capacity for heat radiation of sunlight is low (R~10—60%). From this it follows that a certain radiation component of the sunlight can penetrate into the interior of the room from the outside and heat it.

However, the heat protective system prevents an emission of the heat from the interior of the room towards the outside. In the range of the "far infrared" (wavelength of the radiation of a black body at room temperature: λ~10 um) the heat protective system in accordance with the invention has a very high (R~95%) reflective capacity. Hereby, the heat radiation in the interior of the room is reflected or the radiation exchange with the utside is strongly reduced as a result of the low coefficients of emission of the coating.

Consequently, the heat protective system is very transmissive for solar energy (room heating) but it prevents the room energy from radiating once again towards the outside.

The invention also relates to a method of producing the multi-layer syst ms in accordance

with the invention which hav the advantag s previously described.

An advantageous further d velopment and improvement of the multi-layer system set forth in the main claim is made possible by the measures set forth in the sub-claims. Moreover, advantageous forms of the method in accordance with the invention are expressed in further sub-claims.

Multi-layer systems in which silver is used as a metal layer and titanium dioxide is used as a dielectric layer are of special advantage, whereby cover layers with higher strength are produced by reactive atomisation (cathode atomisation) in an argon-oxygen-nitrogen-atmosphere. The use of magnetron atomisation in the vapour deposition of the strip is especially preferable due to the high dusting rates which can be achieved.

The cover layer of the multi-layer system in accordance with the invention can either consist of a mixture of the individual compounds (for example TiO_2, TiN or of oxide-nitrides) or the individual compounds can each be applied as individual layers in a separate working operation. This may be achieved technically in a simple manner by a repeated conveyor run. Since the required low layer thickness can be generated by relatively high conveyor speeds, the method is also very economical. A TiO_2 layer in which is embedded a TiO_2TiN layer or a pure TiN layer can be produced for example in this manner. This produces the advantage that a still higher TiN component can be incorporated in a very thin layer. In this way, the desired protective effect can be increased still further.

In addition to the production of cover layers with homogeneous distribution (mixtures of the compounds TiO_2, TIN, TiO_2TiN) or pure layers of these compounds, there exists the further possibility of increasing the resistance to corrosion therein by producing the metal oxide layer, for example TiO_2 layer sub-stoichiometrically, that is to say with a reduced oxygen content. Sub-stoichiometric layers are also known *per se* in the vapour deposition art for titanium oxide. These layers have the property that they become oxidized under the effect of oxygen, for example due to the access of air. The sub-stoichiometric layer in accordance with the invention does not exhibit this effect. Due to its structure and composition, it is stable so that no oxidation takes place due to the action of atmospheric oxygen alone. This can only take place by the action of stronger oxidizing media, such as for example ozone.

A TiO_x layer where x=1.60—1.98 is of special advantage. In that case, the absorption of the room radiation is ind ed increased insignificantly by 0.5—1% but the influence on the metal layer of an oxidizing substance defusing into it is reduced by reaction with the metal titanium in the TiO_x layer. Apparently, an isolation of the defusion paths and with it the desired corrosion protection is apparently achieved by this reaction, that is to say a subsequent oxidation does not take place in the pur metal layer but takes place as a result of the imperfections in the dielectric lay r.

An additional effect for improving the resistance to corrosion can be produced in the layer system according to the invention by a sub-stoichiometric formation of the titanium dioxide component.

The oxides of titanium, silicon, tantalum, zirconium are especially suitable as metal oxides as well as metal sulphides such as ZnS.

Drawing

Embodiments of the invention are illustrated in the drawing and are described in detail in the following specification. Figure 1 shows a multi-layer system comprising a dielectric layer in accordance with the invention on both sides of the metal layer on a carrier, Figure 2 shows a multi-layer system comprising a dielectric layer which is itself composed of a multiple layer and Figure 3 is an embodiment with a further cover layer on the back of the foil.

Description of the Invention

The multi-layer system illustrated in Figure 1 consists of a carrier 11, for example a 50 um thick polyester foil, to which are applied the dielectric layers 12, 14 and the metal layer 13. The carrier is, for example, arranged on the side facing away from the room. In that way, the absorption in the carrier of the room radiation is prevented. However, as already referred to above, another arrangement (cover layer towards the outside) can also be advantageous (a lower emission capacity of the cover layer). The electrically conducting metal layer 13 preferably consists of silver and is incorporated between two dielectric layers. However, also gold, aluminium or copper are suitable for the metal layer.

Basically there are three kinds of construction of the multi-layer system in accordance with the invention:

a) Fig. 1

The cover layer 12, 14 to be applied to the metal layer 13 is produced in one working operation, for example by cathode vaporization. In this case, it consists of a (homogeneous) mixture of the compounds metal oxide (e.g. TiO_2), metal nitride (e.g. TiN) and if present oxide nitride (e.g. TiO_2TiN). The metal layer 13 is either embedded on both sides in a cover layer 12, 14, wherein a polyester foil or glass, for example, can serve as a carrier 11. However, the metal layer 13 can also be applied directly to the carrier 11 and only provided on one side with a cover layer 14.

The technical and chemical data (construction) of th metal layer 13 and the cover lay r 12, 14 are as follows:

1. M tal layer: mass coating with silver m_{Ag}=8—14 ug/cm², pr ferably 11 ug/cm². The measured square resistanc of the layer which is preferably used amounts to 7Ω.
2. Cover layer: the entire mass coating with titanium for both layers 12 and 14 amounts

to m_{Ti}=8—16 ug/Cm², preferably 12 ug/cm². Of the entire titanium coating, half is shared respectively by the layers 12 and 14.

Furthermore, the dielectric layers according to the invention also include oxygen and nitrogen in the form of oxides, nitrides and oxide nitrides in the following ratios by weight

60—70 weight % titanium
2—20 weight % nitrogen and
10—40 weight % oxygen.

For the layer which is preferably used a composition results of

65.4 weight % titanium
12.7 weight % nitrogen
21.9 weight % oxygen.

b) Fig. 2:

The cover layer to be applied to the metal layer consists in its turn of a multi-layer system wherein the layers are produced by separate working operations in one or more runs through the atomising equipment. The following construction of the cover layer to be applied to, for example, one silver layer on one side or both sides is possible:

TiO_2 layer—TiN layer—TiO_2 layer

or

TiO_2 layer—TiO_2–TiN layer—TiO_2 layer.

The following data are essential:

With the multiple layer, the titanium content is divided with each third in one of the three layers, that is to say the mass coating with titanium amounts in each layer to m_{Ti}=1.3—2.7 ug/cm², preferably 2 ug/cm².

The nitride containing layer can consist of pure titanium nitride in a stoichiometric composition or, as set forth above, of a mixture of titanium oxide and titanium nitride. However, in this case, at least 50% of the titanium must be present in nitride form. The optical effect of the multiple layer corresponds to that of the single layer with homogeneous distribution of the components.

In Figure 2, the first dielectric multiple layer 22—24 is applied to the plastics carrier 21 (polyester foil). It consists, for example, of a TiO_2 layer 22, 24 in which is embedded a TiO_2TiN layer 23 or even a pure TiN layer. Moreover, there is a pure metal layer 25 (e.g. a silver layer) which is covered by a further dielectric multiple layer 26—28. The layer 26—28 corresponds as regards its construction to the layer 22—24.

c) Fig. 3:

A transmission factor f about 84% in the visible spectral range can be achieved with a layer construction according to Figur 1 with, for example, a pur TiO_2-Ag-TiO_2 layer. Th losses t the extent of 16% r sult from r flection at the boundary surfac s as a r sult f incomplete adaptation and absorption in the carrier foil 11 and in the various layers. During self-supporting use of the foil 11, a shar of about 5% (refractive index of the polyester foil n=1.6) f th reflection occurs at the uncoated side of the foil.

The transmission factor of the heat protective foil is still further increased with the arrangement according to Figure 3.

The heat protective foil arrangement has a demirroring layer (32) on the back of the foil (see Figure 3) which makes possible the optical matching to the medium adjacent to that side of the layer. With a foil 31 stretched in air, the reflection at the boundary surface can be reduced in this manner by about 4%. The transmission factor rises from 84 to 88%.

Furthermore, the layers 33—35 can be constructed according to the embodiments a) or b).

However, a traditional cover layer could also be used for the embodiment according to Figure 3.

The nitrogen component in the dielectric cover layer on the pure metal layer is essential for the increased resistance to corrosion phenomena.

Examples of the method for producing such foils are described in the following:

Example 1 (see Fig. 1):

A TiO_2TiN layer is applied to a 15 um polyester foil 11, 21 (carrier foil) by the conveyor method with the aid of a reactive magnetron atomisation. The partial pressures of the reaction gas are $p_{AR}=5 . 10^{-4}$ mbar, $p_{O2}=3 . 10^{-4}$ mbar, $p_{N2}=3 . 10^{-4}$ mbar. The dusting rate amounts to 140 nm/min with a conveyor speed of 0.5 m/min. A silver layer is sprayed on at a rate of 100 nm/min with an argon partial pressure of $p_{AR}=1 . 10^{-3}$ torr. Thereafter, the second TiO_2TiN layer is provided as set forth above.

Example 2 (Fig. 2):

For producing a dielectric multiple layer with a plurality of individual layers, the carrier 21 is moved many times past the cathode in different residual gas atmospheres. Moreover, the conveyor speed is so selected that just the required total layer thickness is achieved.

Then, with a nitrogen partial pressure of $p_{N2}=5 . 10^{-4}$ mbar, a TiN layer, for example, is produced during a mass coating as before. Then a TiO_2 layer is produced by atomisation in an argon-oxygen mixture at $p_{O2}=5 . 10^{-4}$ mbar and the thickness of which is adjusted by varying the speed of the conveyor or the atomising rate.

Thereafter, a silver layer is produced in the manner already described (see Example 1) and then a further TiO_2 layer and finally a further TiN layer.

A TiO_2TiN layer or a pure TiN layer can be mbedded in a TiO_2 layer, according to Example 2, in order to form the dielectric cover layer (multiple layer system).

Example 3:

For pr ducing a sub-stoichiometric TiO_x layer the oxygen-partial pressure P_{O2} is reduced by 15%

with r spect to the pressur n cessary for th stoichiometric composition. In that case, the absorption of th layer increases independently of the wavelength by 1%. The remaining production requirements proceed according to Examples 1 and 2.

Example 4 (Fig. 3):

The heat protective foil (see Figure 3) consists of layers 33—35 according to the examples a) or b) (see Figures 1 and 2). A $\lambda/4$ magnesium fluoride layer 32 which corresponds to a layer thickness of about 900 Å, is applied to the back of the foil by a further process step (in the same or a separate run). The transmission of the entire system attains 88%.

Claims

1. A multi-layer system for heat protective application, characterised by a high reflective capacity in the far infrared spectral range and a high transmission capacity in the visible spectral range and in the near infrared spectral range, comprising a carrier, a metal layer such as silver, gold, aluminium, copper or the like and at least one dielectric cover layer applied to the metal layer and which includes a metal-nitrogen compound wherein the cover layer or the metal layer can be connected to the carrier.

2. A multi-layer system according to claim 1, characterised in that, the cover layer consists of a mixture of metal oxide and metal nitride.

3. A multi-layer system according to claim 2, characterised in that, the cover layer consists of a mixture of titanium dioxide and titanium nitride.

4. A multi-layer system according to claim 1 or 2, characterised in that, the cover layer consists of a mixture of metal oxide, metal nitride and oxide-nitrides.

5. A multi-layer system according to claim 4, characterised in that, the cover layer consists of a mixture of titanium dioxide, titanium nitride and titanium-oxide-nitride.

6. A multi-layer system according to claim 1, characterised in that, the cover layer is formed as a multi-layer system and consists of a metal nitride layer and at least one metal oxide layer.

7. A multi-layer system according to claim 6, characterised in that, the cover layer consists of at least one titanium dioxide layer and a layer of a titanium dioxide-titanium nitride-mixture.

8. A multi-layer system according to claim 1, characterised in that, the cover layer is formed as a pure titanium nitride layer.

9. A multi-layer system according to one or more of the preceding claims 1 to 5, characteris d in that, the cover lay rs can be applied with a sub-stoichiometric oxygen cont nt.

10. A multi-layer system according to claim 5 or 6, characterised in that, the cover layer is applied from a TiO_x layer when x=1.60—1.98.

11. A multi-layer system according to on or more of the preceding claims, charact rised in that, a transpar nt plastics, especially a polyester foil, is provided as a carrier.

12. A multi-layer system according to one or more of the preceding claims, characterised in that, glass is provided as a carrier.

13. A multi-layer system, especially according to one of the preceding claims, characterised in that, a further dielectric layer is applied to the back of the carrier.

14. A multi-layer system according to claim 13, characterised in that, the layer is formed as a $\lambda/4$ magnesium fluoride layer with a layer thickness of about 900 Å.

15. A method of producing a multi-layer system having a high reflective capacity in the far infrared spectral range and a high transmission capacity in the visible spectral range and in the near infrared spectral range comprising a metallic layer such as silver, gold, aluminium, copper and at least one dielectric cover layer, characterised in that, the dielectric cover layer is applied to the metal layer in an argon-oxygen-nitrogen-atmosphere.

16. A method according to claim 15, characterised in that, a first metal oxide-metal nitride layer (oxide nitride) is applied to a carrier foil with the aid of a reactive magnetron atomisation then a pure metal layer is applied and finally a further metal oxide metal nitride layer is applied.

17. A method according to claim 16, characterised in that, a TiO_2-TiN layer (12), a silver layer with a mass coating of 8—14 ug/cm², especially 11 ug/cm² and a further TiO_2-TiN layer are applied successively to a polyester foil about 50 um thick, wherein the dielectric layers have the following composition in weight percentage:

titanium	60—70 especially 65 weight %
nitrogen	2—20 especially 13 weight %
oxygen	10—40 especially 22 weight %.

18. A method according to claim 15, characterised in that, first of all a metal oxide layer then a metal oxide-metal nitride layer and finally a further metal oxide layer are applied to at least one side of the metal layer.

19. A multi-layer system for heat protective application, substantially as herein described with reference to Figure 1, Figure 2 or Figure 3 of the accompanying drawings.

20. A method of producing a multi-layer system for heat protectiv application, substantially as herein described.

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